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(54) PROCESS FOR THE PREPARATION OF α-METHYLSTYRENE

(71) We, PROGIL, a French Body Corporate, of 77, Rue de Miromesnil, Paris 8e, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for obtaining pure alphamethylstyrene (hereinafter referred to as "alpha-Mes") from organic fractions rich in dimethylphenylcarbinol (hereinafter referred to as "DMPC") but contaminated with impurities.

DMPC is an important intermediate product obtained in the crude state during the manufacture of phenol and acetone from cumene hydroperoxide or during the epoxidation of olefins or allyl alcohol with the above hydroperoxide. The DMPC is generally a rather impure product, contaminated principally with cumene, acetophenone, butylbenzenes, phenol and traces of non-volatile organic materials.

It is known to dehydrate DMPC to give alpha-Mes, the dehydration being performed either in the liquid phase in the presence of a catalyst, for example sulphuric acid, an alkali bisulphate or a non-volatile carboxylic acid, or in the vapour phase in the presence or absence of a catalyst such as granular metal oxides for example titanium dioxide. However, by these techniques, alpha-Mes of at least 99% purity cannot be obtained if the DMPC contains more than 1% of impurities such as those enumerated above, since the latter appear in the alpha-Mes which is therefore unsuitable for its conventional use in homopolymerisation and copolymerisation.

A process has now been found which allows an impure DMPC such as that described above to be converted easily and directly in the liquid phase into alpha-Mes of more than 99.5% purity. This is achieved by vacuum-distilling the crude DMPC to remove the volatile impurities of boiling point below that of acetophenone and then dehydrating the bottoms fractions so obtained, in the liquid phase and in the presence of a known catalyst, with simultaneous distillation of water and alpha-Mes, the latter then being optionally dephenolated by washing with an alkali hydroxide.

The process of the invention is therefore one for preparing alphamethylstyrene having a purity greater than 99.5%, the process comprising (a) vacuum distilling crude dimethylphenylcarbinol containing acetophenone to give a bottoms fraction enriched with dimethylphenylcarbinol and acetophenone, (b) subjecting the bottoms fraction, in a single stage, to dehydration in the liquid phase and in the presence of a non-volatile catalyst, and to distillation, to give a distillate fraction comprising water and alphamethylstyrene, and (c) separating alphamethylstyrene from the water by decantation.

Stage (a) can suitably be carried out in a conventional column containing the equivalent of at least 10 theoretical plates and operating under reduced pressure, generally 50 to 120 mm.Hg, and preferably under a reflux ratio of 5 to 15. Under these conditions, the volatile impurities, for example cumene and butylbenzenes, are easily removed as the distillate; the bottoms fraction comprises DMPC, acetophenone, phenol and traces of non-volatile products.

In stage (b), the bottoms fraction is dehydrated in the presence of a catalyst, for example concentrated aqueous sodium bisulphate, preferably in an amount of 0.01 to 0.5% of bisulphate, based on the weight of the total feed. The operation is suitably carried out under atmospheric pressure in a stirred reactor at 180 to 230°C. The dehydation reactor is suitably surmounted by a distillation column having at least 10 theoretical plates; the more volatile water and alpha-Mes is separated by distillation from the acetophenone and non-volatile products. Preferably, the temperature at the head of the column is 140 to 160°C. and a reflux ratio of at least 2 is maintained therein by means of the upper organic phase from decantation stage (c). Under these conditions, the dehydration of the DMPC is practically instantaneous and complete. The yield of

alpha-Mes obtained in the distillate is greater than 95%; less than 0.5% of alpha-Mes polymers are formed.

The alpha-Mes and the water in the distillate are separated by simple decantation. Depending on the origin of the crude DMPC used as the starting material, the alpha-Mes may contain small amounts of phenol, which can be extracted by an alkaline wash with an aqueous alkali hydroxide. After the alkaline wash has been performed, it is generally necessary to free the alpha-Mes from traces of water suspended therein. This operation can be carried out in a simple coalescer.

The process of the invention is advantageously performed continuously.

The alpha-Mes obtained by the process, being of high purity (about 99.9%), is suitable for use in the manufacture of homopolymers and copolymers or in a hydrogenation process to give cumene intended for the manufacture of pure cumene hydroperoxide.

The invention is illustrated by the following Example; a suitable apparatus for the process is shown in the Figure.

EXAMPLE

To distillate column (A) of 15 plates, operating under 70 mm.Hg, with a bottom temperature of about 130°C. and reflux ratio of about 10, was fed through the pipeline (1), at the rate of 200 kg/hr., crude DMPC obtained from an olefin epoxidation process and having the following composition (% weight):

volatile hydrocarbons	0.2
cumene	6.8
butylbenzenes	0.2
alpha-Mes	0.5
acetophenone	2.9
DMPC	87.2
phenol	0.3
non-volatile products	1.9

The distillate, consisting essentially of cumene and the butylbenzenes, obtained at the top of the column was removed through pipeline (2); the bottoms fraction, representing 90% of the initial charge, was withdrawn through line (3) and had the following composition (% weight).

alpha-Mes	0.7
acetophenone	3.2
DMPC	93.7
phenol	0.3
non-volatile products	2.1

The bottoms fraction was continuously introduced at the rate of 180 kg/hr. into a dehydration reactor (B) containing acetophenone and maintained at 200°C., to which, at the same time, was also supplied through pipeline (4) 40% aqueous sodium bisulphate at the rate of 0.3 kg. of salt per ton of crude stripped DMPC. The reactor had a stirring system and was surmounted by a distillation column (C) equipped with 10 plates and operating under atmospheric pressure at a head temperature of 151—2°C., with a reflux ratio of 2 obtained by adding organic phase from the decanter (D).

The acetophenone and the non-volatile products were withdrawn at the bottom of the reactor (B) through the pipeline (5); a mixture of alpha-Mes and water of dehydration was recovered, as distillate, through line (6) and was passed into the decanter (D) to give, in a yield of 98%, an upper phase of alpha-Mes, of which a small fraction was recycled through line (7) into the column (C) by way of reflux. The alpha-Mes was free of acetophenone and alpha-Mes dimers and contained 0.18% of phenol.

To further purify the product, the alpha-Mes was passed through pipeline (8) into dephenolation tank (E) to which 10% aqueous sodium hydroxide was fed through pipeline (9). The upper phase from tank (E) was then passed through line (10) into a coalescer (F) wherein any fine water droplets remaining in suspension were removed.

Working continuously under the above conditions, 166 kg/hr of alpha-Mes of purity 99.85% (as determined by chromatographic analysis) were obtained.

WHAT WE CLAIM IS:—

1. A process for preparing alphamethylstyrene having a purity greater than 99.5%, the process comprising (a) vacuum distilling crude dimethylphenylcarbinol containing acetophenone to give a bottoms fraction enriched with dimethylphenylcarbinol and acetophenone, (b) subjecting the bottoms fraction, in a single stage, to dehydration in the liquid phase and in the presence of a non-volatile catalyst, and to distillation, to give a distillate fraction comprising water and alphamethylstyrene, and (c) separating alphamethylstyrene from the water by decantation.

2. A process according to claim 1 wherein the crude dimethylphenylcarbinol is contaminated with cumene, butylbenzenes, acetophenone, phenol and/or non-volatile organic materials.

3. A process according to claim 1 or 2 wherein the crude dimethylphenylcarbinol is derived from the preparation of phenol and acetone from cumene hydroperoxide or is derived from the epoxidation of an olefin or allyl alcohol by cumene hydroperoxide.

4. A process according to any one of the preceding claims wherein stage (a) is performed at a pressure of 50 to 120 mm. of mercury.

5. A process according to any one of the preceding claims wherein stage (a) is

performed at a reflux ratio of 5 to 15.

6. A process according to any one of the preceding claims wherein the dehydration is performed at 180 to 230°C.

7. A process according to any one of the preceding claims wherein the catalyst is sodium bisulphate.

8. A process according to claim 7 wherein the amount of catalyst is 0.01 to 0.5% by weight based on the weight of the bottoms fraction.

9. A process according to any one of the preceding claims wherein the distillation in stage (b) is performed at atmospheric pressure and at a head temperature of 140 to 160°C.

10. A process according to claim 9 wherein the distillation is maintained at a reflux ratio of at least 2 by means of alphamethylstyrene derived from stage (c).

11. A process according to any one of the preceding claims wherein the alphamethylstyrene from stage (c) is washed with an aqueous alkali.

12. A process according to claim 1 substantially as described in the Example.

13. Alphamethylstyrene prepared by a process according to any one of the preceding claims.

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1 SHEET

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